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(54) DEPOLYMERIZATION OF CELLULOSE ETHERS BY ELECTRON IRRADIATION

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Water-soluble cellulose ethers are commercially prepared by selective depolymerization of very high molecular weight natural cellulose such as cotton linters or wood pulp by chemical and physical means. In preparing sodium carboxymethyl cellulose and alkyl cellulose ethers, natural cellulose is treated with alkali to reduce its molecular weight and solution viscosity prior to carboxymethylation or alkylation. Yet some applications require a greater solubility than can be economically achieved by chemical treatment. The increased solubility adversely affects normal purification methods.

Irradiation depolymerization of an essentially dry solid cellulose ether is particularly suitable for preparing products the 2 weight percent aqueous solutions of which have a viscosity below 100 cps. at 20°C.

The non-uniform dose within a solid irradiated sample causes several operating problems. If a sample thickness is adequate to absorb all the radiation energy, various portions of the sample receive widely different doses and a non-uniform product is obtained. If a very thin sample is used, a significant portion of the radiation energy is lost.

It has now been found and the discovery forms the basis for the present invention that cellulose ethers can be very effectively depolymerized by exposing the substantially dry solid ether to a beam of accelerated electrons in a process wherein substantially all of the radiant energy is absorbed by the use of a layer or bed of the cellulose ether having a depth approximately the same as the penetration depth of the beam.

In accordance with the present invention there is provided a process for depolymerizing a water soluble cellulose ether which process comprises irradiating a layer of a free flowing, particulate, water-soluble cellulose ether, said layer having a uniform depth adjusted to within 10 percent of the penetration depth of the beam, with a beam of accelerated electrons and thoroughly blending the thus treated cellulose ether.

Particularly good results are obtained when the electron beam is accelerated by a 0.3 to 10 million electron volt (Mev) accelerator.

While substantially any particulate cellulose ether can be depolymerized in this manner, the process of the invention is especially adapted to the depolymerization of nonionic alkyl cellulose ethers such as, for example, methyl cellulose ether and hydroxypropyl methyl cellulose ether. In a more preferred embodiment of the invention, hydroxypropyl methyl cellulose, the 2 weight percent aqueous solution of which has a viscosity at 20°C. of 50 centipoises (cps) can be irradiated preferably in a layer containing 1.0 ± 0.1 g/cm^3 with a beam of 2.0 Mev electrons to provide an irradiated cellulose product, the 2 weight percent aqueous solution of which has a viscosity at 20°C. of 2 to 25 cps.

This invention provides for more efficient utilization of the irradiation energy in reducing the molecular weight of a free-flowing, particulate cellulose ether as evidenced by a lower solution viscosity. By using an irradiation thickness about equal to the penetration range of the electron beam, and blending the irradiated ether in a free-flowing particulate form, essentially complete utilization of the irradiation energy is achieved and a product having properties of essentially uniform irradiation is achieved.

Other advantages will become apparent from

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the following description and the accompanying drawings in which Figure 1 is a depth-dose curve for 2 Mev electrons, Figure 2 is a penetration vs. acceleration voltage curve, and Figure 3 is a cross-sectional view of one embodiment of a device suitable for the present process.

Referring to Figure 1, the radiation dose delivered by an electron beam to a solid material varies with the depth of beam penetration. It is proportional to the energy of the beam and inversely proportional to the density of the material. For 2.0 Mev electrons, the relative radiation dose increases from 60% of the maximum at the entrance surface of the irradiated material to 100% at 1/3 the maximum penetration range and then decreases rapidly to 0 at the maximum range. Similar curves have been determined for electrons with other initial energy levels.

To reduce dose variation within a sample, normally the sample thickness or depth (D) is adjusted so that the entrance and exit surfaces receive an equal radiation dose. With 2 Mev electrons as shown in Figure 1, the entrance-exit dose in 60% of the maximum dose. The energy penetrating beyond the exit surface is wasted. For 2 Mev electrons the waste energy represented by the shaded area W amounts to 16% of the energy incident on the material.

Figure 2 expresses the penetration depth or range of the accelerated electrons in g/cm^2 as a function of the acceleration voltage. For incident electrons of 0.3—15 Mev, the penetration range is 0.5—0.6 g/cm^2 Mev. More precisely the penetration range for preferred operating voltages (E) of 0.5—10 Mev is given by the formula:

$$R(g/cm^2)=0.542E-0.133$$

(Kohl e.a., "Radioisotope Applications Engineering", New York, 1961, p. 430).

Figure 3 illustrates an apparatus suitable for the present process. In this embodiment, the free-flowing particulate cellulose ether 2 is fed from a vibrating feeder 4 onto a continuous conveyor belt 6 to form a substantially uniform layer 8 of the cellulose product on the belt. The thickness of the layer is adjusted to 100 ± 10% of the effective range of the accelerated electron beam 10. The belt carries the layer of cellulose ether through the accelerated electron beam 10. The beam is produced by a generator (not shown) and spread or diffused, for example, by passing through a flared scanner 12 and a thin metal foil window 14, before impinging on the layer of cellulose product. The electron beam is absorbed by the layer of solid particulate cellulose ether passing through the beam. The irradiated product 16 is transferred as a free-flowing particulate stream into a collecting hopper 18 having a pneumatic conveyor outlet line 20 to convey the irradiated ether to another unit 22 for storage, further processing or packaging.

Since the depth of the layer of solid particulate cellulose ether passing through the electron beam is about equal to the penetration range of the accelerated electrons, an overall energy absorption efficiency of 96% or better is obtained. The exact efficiency will depend on the amount of overscan used in irradiating the ether.

It has been found that transfer of the irradiated cellulose ether from the conveyor belt to the collecting hopper as a free-flowing, particulate stream and subsequent transfer to storage by a pneumatic conveyor line provides the thorough blending essential to obtaining a final bulk product having an essentially uniform average irradiation dose. However, a blender designed to handle the particulate solids can also be incorporated in the process line subsequent to the irradiation station.

The improved process can be used to depolymerize a variety of free-flowing particulate cellulose ethers. Particularly suitable are water-soluble cellulose ethers obtained by chemical modification of wood and cotton cellulose. Typical of such chemically modified cellulose ethers are cellulose ethers including C_1—C_4 alkyl and hydroxyalkyl ethers such as methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose, and hydroxyethylmethylcellulose; carboxyalkyl cellulose including carboxymethylcellulose; methylcarboxymethylcellulose, hydroxypropylcarboxymethylcellulose, carboxymethylhydroxyethylcellulose and ethylhydroxyethylcellulose ethers.

It is essential that these cellulose ethers be in a free-flowing, particulate form so that a substantially uniform layer can be prepared for irradiation and thereafter readily blended to obtain a desired average irradiation dose. Granular and powdered forms can be used with an ether having a particle size finer than 10 mesh (U.S. Standard Sieve Scale) being preferred.

The moisture content of the cellulose ether is not critical, provided that the particles are free-flowing and non-agglomerating when irradiated. With an alkylcellulose ether, a nominally dry and free-flowing product can contain up to 4% by weight water, but a moisture content less than 2% by weight is usually desirable.

The process is particularly suitable for reducing the viscosity of a water-soluble cellulose ether having a viscosity of 100—4,000 cps. as a 2 weight percent aqueous solution at 20°C. to less than 100 cps. and preferably to 2—25 cps.

Machines capable of producing a beam of 0.3—10.0 Mev electrons are commercially available and include cascade, Van de Graaff, and linear accelerators. The radiation time will vary from a few seconds to several minutes

depending on the strength of the radiation source and the total dose required to obtain the desired degree of depolymerization. With 0.5—2.0 Mev electrons, a radiation dose of up to 6 megarad/pass can be used without overheating the cellulose ether. For higher doses multipass irradiation is often desirable.

To illustrate further the present invention, the following examples are given. Unless otherwise stated, all parts and percentages are by weight. All viscosities were determined as a 2 weight percent aqueous solution at 20°C.

EXAMPLE 1

Radiation of Cellulose Ethers with 2.0 Mev Electrons

Samples of powdered water-soluble hydroxypropylmethylcellulose were weighed into open dishes to give sample thicknesses of 0.18—1.50 g/cm². The samples were then irradiated with 2.0 Mev electrons from a Van de Graaff generator by passing the sample dishes through the electron beam in a direction normal to the beam. Beam currents of 250 μa were used with a beam scan of 41 cm at the sample level. For samples having a thickness less than 0.66 g/cm², aluminum filters were interposed between the beam exit window and the sample surface to bring the sample thickness to the proper position on the 2.0 Mev electron depth-dose curve (Figure 1). The 2.0 Mev electrons have a penetration range of 1.0 cm/g².

After irradiation, the powdered samples were individually blended by dry mixing until homogeneous. Then the 2 weight percent aqueous solution viscosities of the irradiated samples were determined at 20°C. using calibrated Ubbelohde viscosimeters (ASTM Method D—1347—56).

Experimental results with samples of hydroxpropylmethyl cellulose having an initial viscosity of 50 cps. and 400 cps. are given in Tables 1—4.

TABLE 1

Radiation of 50 cps. Cellulose Ether

Sample No.	Thickness (g/cm²)	Av. Dose (Mrad)	Dose Spread Min. — Max.	Final Viscosity
1—1	0.18[a]	6	60—63%	10.7 cps
1—2	0.66	6	60—100%	10.2 cps
1—3	1.00	6	0—100%	9.9 cps
1—4	0.18[a]	10	60—63%	4.8 cps
1—5	0.66	10	60—100%	6.7 cps
1—6	1.00	10	0—100%	6.1 cps
1—7	1.00	10	0—100%	6.1 cps

[a] Aluminum filter used.

TABLE 2

Radiation of 400 cps. Cellulose Ether

Sample No.	Thickness (g/cm²)	Av. Dose (Mrad)	Dose Spread Min. — Max.	Final Viscosity
2—1	0.18[a]	6	60—63%	19.1 cps
2—2	0.66	6	60—100%	16.8 cps
2—3	1.00	6	0—100%	16.1 cps
2—4	0.18[a]	10	60—63%	6.5 cps

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TABLE 2 (continued)

Sample No.	Thickness (g/cm²)	Av. Dose (Mrad)	Dose Spread Min.—Max.	Final Viscosity
2—5	0.66	10	60—100%	8.9 cps
2—6	1.00	10	0—100%	5.6 cps
2—7	1.00	10	0—100%	9.0 cps
2—8	1.00	15	0—100%	6.7 cps
2—9	1.10	15*b*	0—100%	11.9 cps
2—10	1.20	15*b*	0—100%	16.3 cps
2—11	1.50	15*b*	0—100%	39.8 cps
2—12	0.6	20	60—100%	3.0 cps
2—13	0.8	20	35—100%	2.9 cps
2—14	0.9	20	18—100%	3.8 cps
2—15	1.0	30	0—100%	2.9 cps

a Aluminium filter used.

b Dose for top 1 g/cm². Lower portion unirradiated.

Table 1 illustrates effective radiation depolymerization of a 50 cps. hydroxypropylmethyl cellulose for thicknesses up to 1.00 g/cm², the range for 2.0 Mev electrons. At a thickness of 0.66 g/cm², a thickness at which the radiation dose at the top and bottom surfaces is about the same, the energy absorption efficiency is 85%. By increasing the thickness to 1.00 g/cm², the absorption efficiency is 100%. In terms of a theoretical input of a 500 watt accelerator with a 100% beam utilization and a 75% scanning efficiency, an increase in the thickness from 0.66 g/cm² to 1.00 g/cm² increases the machine output from 55.2 megarad kg/hr to 65.8 megarad kg/hr, an increase of 19%.

Table 2 illustrates a similar increase in efficiency and effective radiation depolymerization of a 400 cps hydroxypropylmethyl cellulose. Note that in the range from 0.18 g/cm² to 1.0 g/cm² the final viscosity is dependent on the dose, but independent of the dose spread and sample thickness. With samples thicker than 1.0 penetration range of the 2.0 Mev, the lower portion of the sample is unirradiated. Because the product is thoroughly blended after irradiation, a small amount of unirradiated product can be tolerated without detrimental effect on the final product. As the spread between initial and final viscosity increases, the amount of unirradiated product that can be tolerated decreases. Thus for optimum utilization of the irradiation energy and product properties, the depth of the radiation sample should be controlled to ±10% of the penetration range of the accelerated electrons.

EXAMPLE 2

Radiation of Cellulose Ethers with 0.5 Mev Electrons

Weighed samples of a free-flowing powdered 400 cps hydroxypropylmethyl cellulose were pressed into thin discs having a thickness of 0.127—0.131 g/cm² for radiation with 0.5 Mev electrons from an ICT—500 accelerator (High Voltage Engineering Corp.) having a penetration range of 0.140 g/cm². The test discs were mounted on a cardboard backing and passed through the 0.5 Mev beam at a rate adjusted to give a desired average dose. The individual samples were then ground and thoroughly blended before viscosity determinations were made.

Typical results shown in Table 3 show an effective and efficient radiation depolymerization using a sample thickness about equal to the penetration range of the accelerated electrons.

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TABLE 3

Radiation with 0.5 Mev Electrons

Sample No.	Thickness (g/cm²)	Av. Dose (Mrad)	Final Viscosity
3—1	0.1280	0	335 cps
3—2	0.1284	4.4	19.7 cps
3—3	0.1279	9.0	10.5 cps
3—4	0.1288	10.4	7.9 cps
3—5	0.1296	12.8	6.9 cps
3—6	0.1289	16.7	5.1 cps

EXAMPLE 3

Radiation of Cellulose Ethers with 1.0 Mev Electrons

Samples of a free-flowing powdered 400 cps. hydroxypropylenethyl cellulose were weighed into aluminum dishes and spread to give a uniform thickness. Radiation with an ICT—1000 accelerator (High Voltage Engineering Corp.) yielding 1.0 Mev electrons with a penetration range of 0.55 g/cm² with average doses ranging from 3—25 Mrad gave irradiated products having final viscosities after blending of 19.7—5.1 cps. The product viscosity was proportional to the average dose. Use of a sample thickness equivalent to the penetration range of the 1.0 Mev electrons resulted in optimum utilization of the radiation energy.

EXAMPLE 4

Radiation of Cellulose Ethers with 8.4 Mev Electrons

Several samples of a free-flowing powdered 400 cps hydroxypropylmethyl cellulose were prepared and irradiated using a nominal 10 Mev electron beam from the Linac microwave linear accelerator at the Midwest Irradiation Center, Rockford, Illinois. Calibration at the time the cellulose ether samples were irradiated indicated a beam with an energy equivalent to about 8.4 Mev. Typical results are shown in Table 4.

TABLE 4

Radiation with 8.4 Mev Electrons

Sample No.	Thickness (g/cm²)	Dose (Mrad)			Final Viscosity
		Top Surface	Exit Surface	Av.	
4—1	2.0	10.8	12.1	14	5.9
4—2	3.0	10.0	6.5	12.3	7.0
4—3	5.0	10.9	0.3	5.4	18.6

EXAMPLE 5

Radiation Conditions

In the preparation of a lower viscosity cellulose derivative by electron beam irradiation of a free-flowing higher viscosity product, the total radiation dose is the critical process parameter. With a free-flowing particulate cellulose ether uniformly blended after radiation, the depth-dose distribution and the molecular weight distribution of the cellulose ether combine to yield a final viscosity that is a reproducible function of the average radiation dose.

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Control of the sample thickness to 100 ± 10% of the effective range of the accelerated electrons provides essentially complete utilization of the radiation energy.

The moisture content and temperature of the cellulose ether when irradiated also have a small effect on the viscosity change for a given dose as shown by typical results in Tables 5 and 6 using a standard hydroxypropylmethyl cellulose.

TABLE 5

Moisture Content (2.0 Mev; 0.66 g/cm²)

Run	Initial Viscosity	% H_2O *a*	Dose Megarad	Final Viscosity
5—1	50.6 cps	0	10	7.4 cps
5—2	50.6 cps	4.3	10	5.8 cps
5—3	50.6 cps	8.2*b*	10	6.5 cps
5—4	392 cps	0	10	8.6 cps
5—5	392 cps	3.9	10	6.9 cps
5—6	392 cps	11.8*b*	10	6.3 cps

a Dried in vacuo (<1μ) for 16 hrs. at room temperature and then known amount of water added.

b Some agglomeration observed.

TABLE 6

Radiation Temperature (2.0 Mev; 0.66 g/cm²)

Run	Initial Viscosity	Temp.*a*	Dose Megarad	Final Viscosity
6—1	56.1 cps	21°C.	6	10.2 cps
6—2	56.1 cps	75°C.	6	9.5 cps
6—3	56.1 cps	125°C.	6	6.7 cps
6—4	392 cps	21°C.	6	16.8 cps
6—5	392 cps	50°C.	6	16.7 cps
6—6	392 cps	100°C.	6	10.6 cps
6—7	3570 cps	21°C.	6	34.6 cps
6—8	3570 cps	100°C.	6	22.0 cps

a. Sample temperature before irradiation.

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WHAT WE CLAIM IS:—

1. A process for depolymerizing a water soluble cellulose ether which process comprises irradiating a layer of a free flowing, particulate, water-soluble cellulose ether, said layer having a uniform depth adjusted to within 10 percent of the penetration depth of the beam, with a beam of accelerated electrons and thoroughly blending the thus treated cellulose ether.

2. A process as claimed in claim 1 wherein the beam is accelerated by a 0.3 to 10 Mev accelerator.

3. A process as claimed in claim 1 or claim 2 wherein the cellulose ether which is irradiated is a non-ionic alkyl cellulose ether.

4. A process as claimed in claim 3 wherein the alkyl cellulose ether is a methyl cellulose ether or a hydroxypropyl methyl cellulose ether.

5. A process as claimed in any one of claims 1 to 4 wherein a cellulose ether, the 2 weight percent aqueous solution of which has a viscosity at 20°C. of 50 centipoises, is irradiated and blended to prepared an irradiated cellulose ether, the 2 weight percent aqueous solution of which has a viscosity at 20°C. of 2 to 25 centipoises.

6. A process as claimed in claim 5 wherein a layer of hydroxypropyl methyl cellulose having a thickness to provide 1.0 ± 0.1 g/cm^2 is irradiated with 2.0 Mev electrons.

7. A process as claimed in claim 1 substantially as hereinbefore described in the specific Examples.

8. A water-soluble cellulose ether whenever obtained by a process as claimed in any one of claims 1 to 7.

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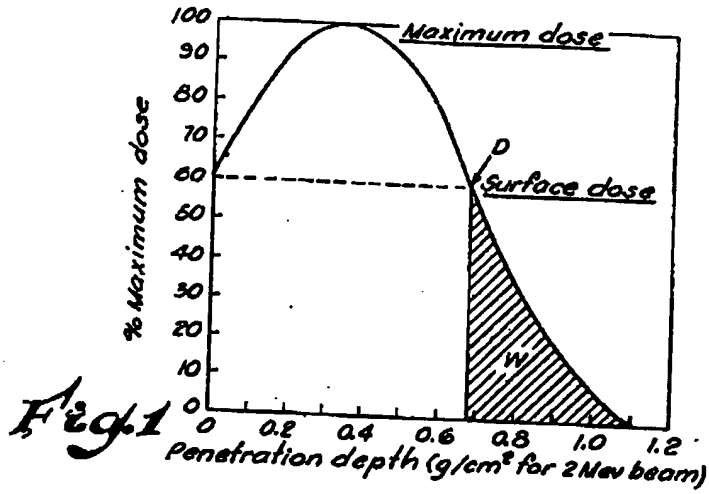

Fig. 1

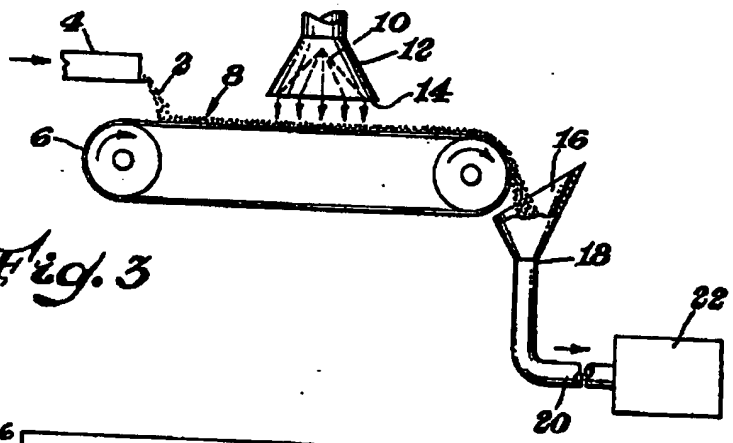

Fig. 3

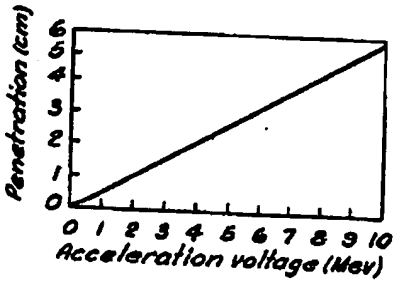

Fig. 2